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An overview of advanced thermoelectric materials

A large amount of our useful energy is being lost as waste heat. Much of this wasted heat is of high grade and occurs in a distributed fashion. Therefore is a compelling need for high-performance thermoelectric materials that can directly and reversibly convert heat to electrical energy [1]. In the past decades, the exploration of high-performance thermoelectric materials has attracted ever-increasing attention both from the energy and environmental fields and with a view to commercial applications. Considering the structural, electronic and compositional complexity of thermoelectric materials, further development would benefit greatly from close collaborations across a large scientific community of chemists, physicists and materials scientists [2,3].

Globally, some groups have been at the vanguard of development in the field of thermoelectrics. We believe that these advances deserve to be highlighted to the broad readers of Journal of Materiomics. For this purpose, we compiled this thermoelectric special issue, which involves high-*ZT* PbTe, SnTe, Cu_2Se, oxychalcogenides (BiCuSeO), $Cu_2CdSnSe_4$, MnTe, half-Heusler, Skutterudites, caged-free Cu-based diamond-like compounds, and $Mg_2Sn_{0.75}Ge_{0.25}$ *etc*. The aspects of this special issue cover strategies of electronic band structures engineering, microstructure designing, nano-structuring, and the first-principles calculations, *etc*.

Many of the key discoveries in thermoelectric materials have been brought forth by fundamental understandings gained from the first-principles investigations. Density functional theory (DFT) provides a framework in which band structure predictions, phase diagrams enabled by cluster expansion methods, and the phase stability of unknown compounds can be calculated. Half-Heusler alloys are an exciting class of thermoelectric materials that have shown great improvements in the thermoelectric figure of merit, *ZT*, during the past 15 years. Recent theoretical work has been summarized and reviewed by C. Uher et al. [4].

Understanding and manipulating of the band structures are important in designing high-performance thermoelectric materials, i.e., the band convergence, the conductive network, dimensionality reduction and high-throughput material screening. J. Yang and W. Q. Zhang et al. summarize and demonstrate the importance of the microscopic perspectives for the optimization and design of novel thermoelectric materials [5], which include Skutterudites and caged-free Cu-based diamond-like compounds, *etc*.

Layered oxychalcogenides (i.e. BiCuSeO) have recently emerged as promising thermoelectric materials. The alternation of ionic oxide and covalent chalcogenide layers found in these materials often results in interesting electronic properties, and also facilitates the tuning of their properties *via* chemical substitution at both types of layers. P. Vaqueiro et al. summarize and highlight some common structure types found for layered oxychalcogenides [6].

Most significant advances in the field of thermoelectrics have been achieved in bismuth or lead chalcogenides, in which a very low thermal conductivity can be obtained *via* hierarchically all-scale phonon scattering and high electrical transport properties through tuning its complex valence band structure. In this special issue, T. J. Zhu and X. B. Zhao et al. report that the approach of forming solid solutions is an effective way to reduce the lattice thermal conductivity and enhance the power factor *via* modifying the band structure in PbTe-based materials [7]. The multi-alloying of Mg and Se in PbTe system could effectively enhance the *ZT*. A maximum *ZT* of ~2.2 at 820 K was achieved in $PbTe_{0.8}Se_{0.2}$ with MgTe, moreover, such large *ZT* values could be also realized in the sample with large dimensions (~200 g, Φ 42 mm × 18 mm), elucidating a realistic prospect of large-scale commercial fabrications. Introducing nano-scale precipitates has been proved to be one of the most effective approaches to lower the thermal conductivity in PbTe–PbS system, which was known as exhibiting an interesting phase separation feature. To explore the precipitating microstructure and its effects on the thermal conductivity evolvement in the Na doped binary PbTe–PbS system, J. Q. He et al. carried out systematic transmission electron microscopy (TEM) observations on the samples with either varying PbS or Na [8].

To date, attentions have been also turned to SnTe which resembles PbTe in many aspects (i.e., rock-salt crystal structure, small band gaps, complex valence band structure, *etc*.). However, severe drawbacks make SnTe be an inferior thermoelectric material, such as intrinsically high carrier concentration, low Seebeck coefficients and high thermal

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conductivities. To predict the potential performance of SnTe, Y. Chen et al. extensively investigated doping effects of Mg, Ca, Sr, Ba, Eu, Yb, Zn, Cd, Hg, and In on the band structures and electrical transport properties of SnTe, which are based on the first-principles density functional theory including spin−orbit coupling [9]. They found that Zn and Cd have most significant band convergence effects that could potentially lead to power factor enhancement. To reduce the thermal conductivity of SnTe, J. T. Xu, G. Q. Liu, and J. Jiang et al. composited SnTe with $AgSbSe_2$ featured by intrinsically low thermal conductivity [10]. The lattice thermal conductivity was decreased to 0.6 W/mK at 820 K *via* an intense phonon scattering by nanostructures, which were supported by high resolution transmission electron microscopy. A high thermoelectric figure of merit *ZT* of 0.92 at 820 K was obtained in $SnTe-AgSbSe_2$ composites.

Similar to lead-free SnTe, chalcogenide MnTe with typical hexagonal NiAs crystal structure was also reported to be a potential candidate for middle-temperature thermoelectric applications. MnTe possesses a large Seebeck coefficient and a low thermal conductivity, but a huge electrical resistivity makes MnTe be an inferior thermoelectric material. To improve the poor electrical resistivity of MnTe, J. Y. Yang et al. found that Cu is an effective dopant that could increase the hole concentration and boost the electrical conductivity of MnTe [11]. A promising maximum *ZT* of 0.55 was achieved in the $Mn_{0.925}Cu_{0.075}Te$ sample at 773 K, which is improved by 35% in comparison to the undoped MnTe.

Quaternary $Cu_2CdSnSe_4$ is another interesting thermoelectric system, X. N. Sun and X.Y. Zhou et al. found that electrical conductivity could be strongly enhanced while preserving the Seebeck coefficient when $Cu_2CdSnSe_4$ nanoinclusions was introduced in the $Cu_2CdSnSe_4$ matrix [12]. In addition, these inclusions significantly reduce the lattice thermal conductivity through scattering phonons with all-scale length due to the polymorphous structure feature of $Cu_2CdSnSe_4$ composites. The concomitant effects lead to a maximum *ZT* of 0.5 at 760 K, which is 65% higher than that of $Cu_2CdSnSe_4$ matrix.

Binary ordered $Cu_{2-\delta}Se$ compounds were recently reported as promising thermoelectric materials due to interestingly ion-liquid like behavior above room temperature. X. Shi, S. A. Danilkin and L. D. Chen et al. report interesting thermal transport behaviors below room temperature. They found that $Cu_{2-\delta}Se$ shows the extraordinary low lattice thermal conductivity below room temperature [13]. Their results reveal the presence of three Einstein modes in $Cu_{2-\delta}Se$ with the lowest two at 2−4 meV in energy. The inelastic neutron scattering measurements and *ab initio* lattice dynamic calculation further confirmed the presence of low energy optic-like vibrations. These localized strongly damped vibrations of copper ions with weak restoring forces are similar to "near phase changing" soft modes. This work suggests a way to further reduce heat conduction in ordered solid materials using an unusual behavior of phonon branches with low energy multi-Einstein optic phonons.

K. Biswas and G. Sheet et al. directly observe the local ferroelectric ordering above room temperature in rocksalt SnTe, which is a topological crystalline insulator. Interestingly, although SnTe is known to stabilize in a ferroelectric ground state (rhombohedral phase) below ~100 K, it is not expected to show any ferroelectric ordering forbidden by its globally centro-symmetric crystal structure at high temperatures [14]. The results make SnTe be an important member of the family of new multi-functional materials, namely, the ferroelectric-thermoelectrics.

Band convergence is one of the most interesting topics in recent studies of thermoelectric. However, its effect on thermoelectric properties is only simply stated as improving band degeneracy. W. S. Liu and Z. F. Ren et al. investigate the effects of band offset on thermoelectric properties of *n*-type $Mg_2Sn_{0.75}Ge_{0.25}$ based upon three-band model, *i.e.*, one light conduction band, one heavy conduction band, and one valence band [15]. The results show that band offset plays a decisive role in controlling the distribution of carriers in two conduction bands, and has significant influence on thermoelectric properties.

We thank all the authors for their insightful and innovative thinking in composing this excellent thermoelectric special issue, which we hope will be helpful in the continued development of high-performance thermoelectric materials and devices.

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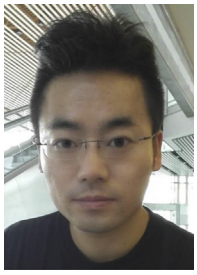

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